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LAID-OPEN PATENT GAZETTE

Patent Laid-Open No. 1986-101247

Laid-Open Date: May 20, 1986

Examination: Unrequested

Title: Carbon monoxide conversion catalyst

Patent application No. 1984-220596

Filing date: October 22, 1984

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Claim

A carbon monoxide conversion catalyst consisting of a mixture of iron oxide, chromium oxide and binders, moulded into a monolithic shape.

Detailed description of the invention

[Industrial field of application]

This invention relates to a monolithic-type catalyst for conversion reaction, which causes water to act on carbon monoxide in order to convert them into carbon dioxide and hydrogen.

[Prior art]

For present civilian-life, city gas is indispensable. In large cities and in the peripheral areas thereof, coal and petroleum and the like which have been being used as raw

materials for city gas hitherto are going to be replaced by liquefied petroleum-gas or liquefied natural-gas. However, in small and medium-sized cities, reformed petroleum-gas has been still a main stream. Because this reformed gas contains toxic carbon-monoxide, it is being strongly desired by various quarters to decrease the content of said carbon monoxide, and in the existing process, carbon-monoxide reduction is being done by the following catalystic reaction:

$$CO + H_2O \xrightarrow{\text{[Catalyst]}} CO_2 + H_2$$

In the abovementioned process, carbon-monoxide conversion reaction is generally being done by using a fixed-bed type reactor full of an iron-oxide - chromium-oxide based catalyst. However, the pressure loss at the time when reformed gas passes through the reactor is large. Moreover, melted solid-substance(s) in steam added at the time of the pulverization and conversion reaction, and rust (corrosion) and so on in the system, are piled up on the catalyst layer, and the pressure loss becomes larger with the lapse of time. Such a problem is caused. The pressure loss at the conversion reactor is causative of increase in the cost for sending (transporting) the gas, and hence, the development of a catalyst for solving the above problem is ~~is~~ being desired in the reformed-gas manufacturing industry.

To achieve this necessity, in the specification of Patent Application No. 1983-025476, proposed was a monolithic-shape catalyst for bringing reformed gas into contact with the surface of a catalyst in such a state as to become parallel with the direction of the flow of said gas. As shown in the example(s)

of this proposal, the tendency of increase in the pressure loss at the catalyst layer has been considerably improved compared with the conventional pillar-like (cylindrical) or pellet-like catalysts.

[Problems to be solved]

In the event that the abovementioned catalyst of the prior application is manufactured by the coating, application or impregnation with effective catalyst-constituents, onto the catalytic base-material formed into any of such shapes as shown in Fig. 1, Fig. 2 and Fig. 3 using, as a material, a woven or fabric consisting of fibers of glass, asbestos, mullite, calcium silicate, etc., kojiellite (phonetically spelled), mullite, etc., the manufacturing process threatens to be cumbersome (1 in Figs. 1 - 3 shows the direction of gas-flow). The inventors eagerly studied the simplification of the manufacturing process, and as a result, they found that if moulded into any of such shapes as shown in Figs. 1, 2, and 3 after adding binders to effective catalyst-constituents, the manufacturing process can be shortened to contribute to manufacturing-cost reduction and that also in connection with the catalytic activity, it is not inferior to the marketed iron-oxide - chrmium-oxide based pellet-catalysts, and this patent has been completed.

[Means for solving problems]

This invention relates to a carbon monoxide conversion catalyst which consists of a mixture of iron oxide, chromium oxide and binders and which has been moulded into a monolithic shape.

The present-invention monolithic-type catalyst for carbon monoxide conversion is produced through the steps (processes) of

using iron oxide and chromium oxide as effective constituents,

mixing (kneading), as binders for moulding the catalyst, one kind or more of such organic substances as methyl-cellulose, vinyl acetate, polyethyleneoxide, polyacrylamide, polyvinylalcohol, starch-powder, etc., one kind or more of glass-fibers, carbon-fibers, metallic fibers, kaolin-fibers, etc., or a mixture consisting of said organic substances and inorganic substances, and

moulding the kneaded mixture as shown in Figs. 1, 2 and 3.

In connection with the iron-oxide - chromium-oxide based catalyst being used as a catalyst for high temperature, this invention is described below based on an example.

Example

$Fe(NO_3)_3 \cdot 9H_2O$

One hundred and fifty-eight grams of $Fe(NO_3)_3 \cdot 9H_2O$ 2 5 5 0 g、$Cr(NO_3)_3 \cdot 9H_2O$ was dissolved in 7500 ml of water and neutralized by 3N-NH_4OH, and the produced sediment of $Fe(OH)_2$ and $Cr(OH)_2$ was filtered and was washed with water until nitric-acid ions disappeared. To a mixture (500 g as oxide) of the obtained $Fe(OH)_2$ and $Or(OH)_2$, water and 40 g of publicly-known methylcellulose as a binder were added and were fully mixed using a kneading machine. Then, by using an extruder, it was moulded so that the shape might be the same as that in Fig. 4 and so that the dimensions (2), (3), (4) and (5) in Fig. 4 might be 7.0 mm, 1.5 mm, 75 mm and 500 mm respectively; and it was baked for 5 hours at 300℃.

With regard to the evaluation of catalyst-performance, pressure-loss and carbon-monoxide conversion rate were measured

based on the test conditions shown in Fig. 1. Also in connection with the marketed Fe-Or catalyst (9.5 mmØ x 8.0 mmh), pressure loss and carbon monoxide conversion rate were measured based on the same conditions, for comparison.

Table 1 Test conditions

Reaction temperature (℃) (Temperature at the inlet of the catalyst layer)	400
GHSV (H^{-1}, Dry Base)	1,000
H_2O/CO mol ratio	3.0
Amount of the catalyst used	Present-invention honey-comb catalyst Marketed product 7.5 cm □ x 50 mmL, 2800 mℓ

Composition of the inlet gas (vol%, Dry Base)

O_2	0.4
N_2	10.6
H_2	58.0
CO	20.0
CO_2	4.5
CH_4	5.6
C_2H_6	0.3
C_2H_4	0.6
C_3H_8	0.1
C_3H_6	0.1

The variation with the lapse of time, of the pressure loss and carbon monoxide conversion rate of the catalyst layer in the example is shown in Fig. 5 and Fig. 6.

As shown in Fig. 5 and Fig. 6, in case of the honeycomb-type catalyst (A) of this invention, the pressure loss is 1/2 ～ 1/5 compared with the marketed Fe-Or based pellet-catalyst (B), and also in connection with carbon-monoxide conversion performance, it is not inferior to others. Therefore, it was verified to be usable as a practicable catalyst.

The catalyst of this invention is effective also for the conversion reaction of aqueous gas for the manufacture of hydrogen for fuel-cells and for the manufacture of hydrogen for ammonia synthesis, and it is not limited to the manufacture of gas.

<u>Simple description of the drawings</u>

Fig. 1 is a view for explaining one shape as an example of plate-like catalysts.

Fig. 2 is a view for explaining one shape as an example of cylindrical catalysts.

Fig. 3 is a view for explaining one shape as an example of honeycomb-type catalysts.

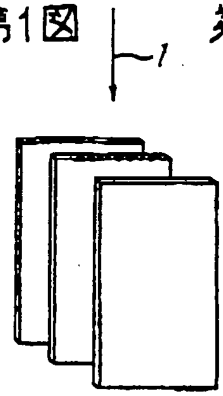
Fig. 4 is a view for concretely showing the shape of the honeycomb-type catalyst mentioned in the example.

Fig. 5 is a view showing the variation of pressure loss with the lapse of time, at the catalyst layer of a conversion reactor full of the catalyst mentioned in the example.

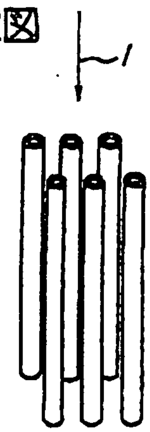
Fig. 6 is a view showing the variation with the lapse of time, of the carbon-monoxide conversion rate of the catalyst mentioned in the example.

(1) in Figs. 1 ~ 3 shows the direction of gas flow; (2) in Fig. 4, pitch (sum of one orifice and the wall thickness); (3), the thickness of the wall; and (4) and (5), outer dimensions.

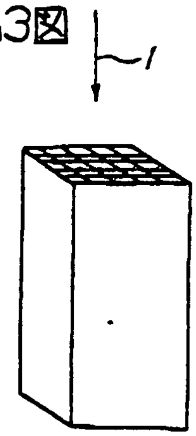
第1図



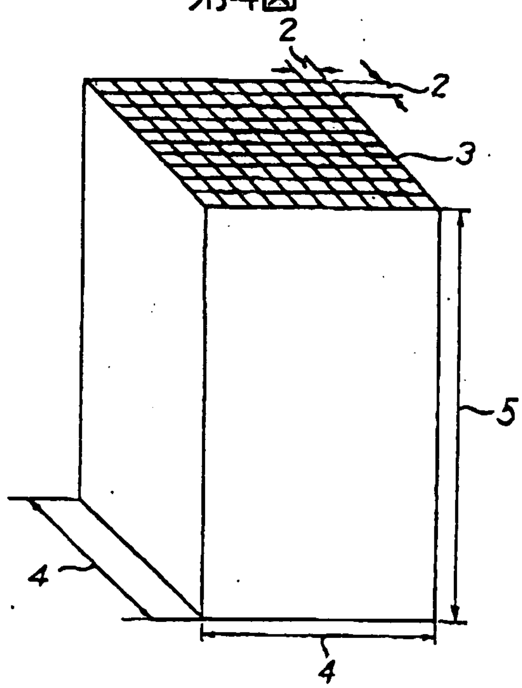
第2図



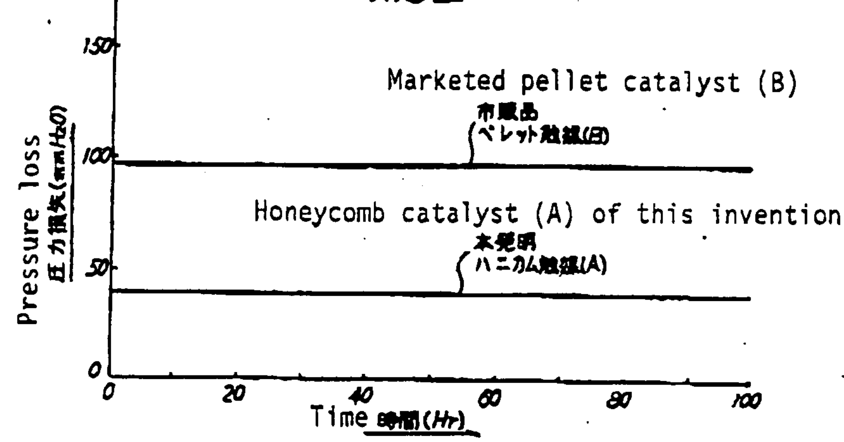
第3図



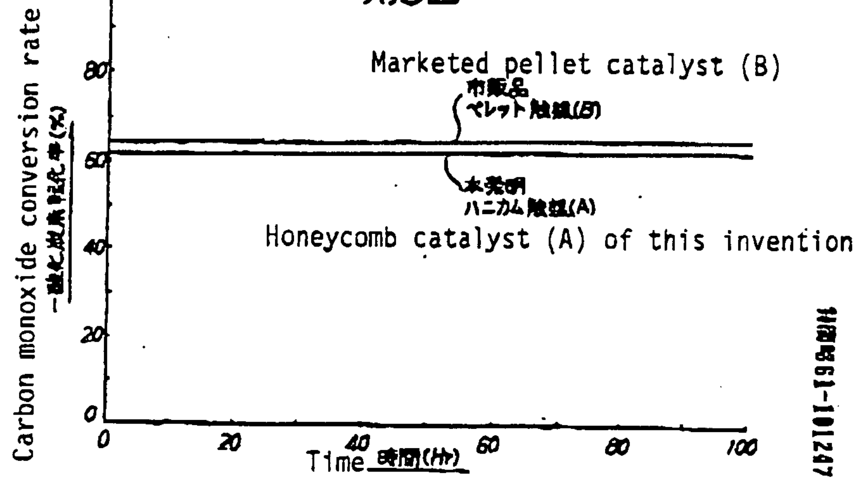
第4図



第5図


Marketed pellet catalyst (B)
市販品
ペレット触媒(B)
Honeycomb catalyst (A) of this invention
本発明
ハニカム触媒(A)
Pressure loss
圧力損失(mmH2O)
0
50
100
150
0
20
40
60
80
100
Time 時間(Hr)

第6図


Marketed pellet catalyst (B)
市販品
ペレット触媒(B)
本発明
ハニカム触媒(A)
Honeycomb catalyst (A) of this invention
Carbon monoxide conversion rate
一酸化炭素転化率(%)
0
20
40
60
80
100
0
20
40
60
80
100
Time 時間(Hr)